



Extractive Spectrophotometric Determination of Bismuth(III) in Water Using Some Ion Pairing Reagents

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Abstract: Two novel and low cost liquid-liquid extraction methods for the separation of bismuth(III) at trace level from aqueous medium have been developed. The two methods were based upon the formation of yellow colored ternary complex ion associates of tetraiodobismuth(III) complex anion, BiI_4^- with the ion-pairing reagent 2,3,5-tetraphenyltetrazoliumchloride ($\text{Tz}^+\cdot\text{Cl}^-$) and 1, 10 phenanthroline (Phen) in sulfuric acid medium. The effect of various parameters *e.g.* pH, organic solvent, shaking time, *etc.* on the preconcentration of bismuth(III) from the aqueous media by the reagent was investigated. The developed colored complex ion associates $[\text{Tz}^+\cdot\text{BiI}_4^-]$ and $[\text{Phen}^+\cdot\text{BiI}_4^-]$ were extracted quantitatively into acetone-chloroform (1:1v/v) and methylisobutylketone (MIBK), respectively. The compositions of the formed complex ion associates $[\text{Tz}^+\cdot\text{BiI}_4^-]$ and $[\text{Phen}^+\cdot\text{BiI}_4^-]$ were determined by the Job's method at 500 and 490 nm, respectively. The plots of bismuth(III) concentration ($0\text{-}17\ \mu\text{g mL}^{-1}$) *versus* absorbance of the associates at 500 and 490 nm were linear with good correlation coefficient ($R^2=0.998$). The developed method of the ion associate $[\text{Tz}^+\cdot\text{BiI}_4^-]$ two methods was applied successfully for the analysis of bismuth in water.

Keywords: Bismuth determination, Ion pairing, Phenanthroline, Ion associate, Wastewater

Introduction

Bismuth presents in oxidation states 3 and 5. Compounds of bismuth(V) are not exist in solution and are very important in view of analytical chemistry¹. Bismuth has been widely used for various industries *e.g.* pigment industry for coloring plastics and paints, batteries² and ceramics^{3,4}, semi-conductors, cosmetic preparations, alloys and as a carrier for U-235 or U233 fuel in nuclear reactors⁵. Its pharmaceutical uses have expanded to peptic ulcer treatments and topical dermatological creams⁶. The use of bismuth in industry and medicine increases therefore, its spread into our environment and the chance of its exposure to organism increased rapidly^{6,7}.

Numerous procedures have been described for the determination of bismuth in pharmaceutical products employing EDTA titration and a variety of indicators *e.g.* pyrocatechol violet, methylthymol blue, eriochrome black T, thioura, xylenol orange, the last being used in the current British Pharmacopoeia method⁸. The tetraiodobismuthate anion has been extracted directly with several onium cations *e.g.* $(C_6H_5)_4P^+$, $(C_6H_5)_4As^+$ and benzyl-dimethylphenyl ammonium into a variety of organic solvents^{9,10}. A liquid - liquid extractive spectrophotometric method has been reported for bismuth(III) determination as tetra-*n*-butylammonium tetraiodo bismuth(III) in chloroform¹¹. Atomic absorption spectrometry and flow-injection hydride generation atomic absorption spectrometry using sodium tetrahydro-carbonate as reductant have been reported for bismuth determination in geological materials¹¹⁻¹³. A new chromogenic reagent 2-(2-arsonophenylazo)-1, 8-dihydroxynaphthaline-3,6-disulphonic acid (2,6-dichloroarsenazo) has been synthesized and successfully used for the spectrophotometric determination of bismuth¹⁴. The present manuscript reports low cost extractive spectrophotometric methods for the separation and subsequent determination of bismuth species in water samples as tetraiodo bismuthate(III) using the ion pairing reagent $Tz^+.Cl^-$ and Phen. The most probable extraction mechanism and composition of the developed complex ion associates were assigned and properly addressed.

Experimental

A Shimadzu double beam UV-VIS (UV-160 7 pc) spectrophotometer with quartz cell (10 mm) was used for recording the UV -Visible spectra and the absorbance of the produced complex ion associates. Infrared (IR) spectra were recorded on a Broker FT-IR spectrophotometer model IFS 66. Perkin Elmer inductively coupled plasma - optical emission spectrometer (ICP- OES, Optima 4100 DC (Shelton, CT, USA) and inductively coupled plasma - mass spectrometer (ICP - MS) Sciex model Elan DRC II (California, CT, USA) were used to measure ultra trace concentrations of bismuth in the aqueous phase after solvent extraction at the optimum operational parameters (Table 1). A Milli-Q waters plus system (Milford, MA, USA) and a thermo fisher scientific Orion model 720 pH Meter were used for water supply and pH measurements, respectively. Microanalyses of C, H, N and I was performed on a Perkin-Elmer 240 C elemental analyzer.

Table 1. ICP-OES operational conditions and wavelength (nm) for bismuth determination*

Parameter	
R _f power (kW)	1050 (900.0)
Plasma gas (Ar) flow rate, L min ⁻¹	15 (15)
Auxiliary gas (Ar) flow rate, L min ⁻¹	0.2 (1.2)
Nebulizer gas (Ar) flow rate, Lmin ⁻¹	0.80 (0.93)
Pump rate, mL min ⁻¹	1.5
Observation height, mm	15
Integration time, s	10
Wavelength, nm	Bi 223.061

*ICP -MS operational parameters are given in parentheses. Other ICP -MS parameters are: lens voltage =9.0; analog stage voltage 1750.0; pulse stage voltage =750; quadrupole rod offset std = =0.0; cell rod offset =-18.0; Discriminator threshold =17.0; Discriminator threshold = -17.0; cell path voltage Std = -13.0 and atomic mass 208.98

Reagents and solutions

All chemicals and solvents used were of analytical reagent grade and were used without further purification. A stock solution (1 mg/mL) of bismuth(III) sub carbonate was prepared

by dissolving an accurate weight (0.13 g) of the salt in 3 HCl (3 mL) then diluted to 100 mL with de ionized water. More diluted solutions of bismuth(III) species were prepared in de ionized water in the presence of few drops of nitric acid as required. Stock solutions (1.5% w/v) of 2, 3, 5 tetraphenyl-2H-tetrazoliumchloride and 1, 10 phenanthroline were prepared in water and the minimum amount of ethanol and completed with de ionized water to the mark, respectively. BDH potassium iodide-ascorbic acid (Poole, England) reagent was prepared by mixing KI (5 g) and ascorbic acid (5) in water and diluting to 100 mL.

General procedures

Extraction with 2, 3, 5 tetraphenyl-2-H-tetrazoliumchloride

An aliquot (3.0 mL) containing 1-15 $\mu\text{g mL}^{-1}$ of bismuth(III) was placed in 100 mL separating funnel (50 mL) and 2 mL H_2SO_4 (1.0 mol L^{-1}), 3 mL of KI - ascorbic acid reagent solution reagent and 1 mL $\text{Tz}^+\cdot\text{Cl}^-$ were added in order. The test solution was diluted to 25 mL with de ionized water and shaken well with 5 mL of the mixed solvent (acetone-chloroform 1:1v/v) for 3 min in the presence of anhydrous sodium sulfate (0.5 g). After separation of the layers, the organic extract was separated out and its absorbance was measured at 500 nm against the reagent blank.

Extraction with 1, 10 phenanthroline

An aliquot (3.0 mL) containing bismuth(III) in the concentration range 0.05 -15 $\mu\text{g mL}^{-1}$ was transferred into separating funnel (50 mL) and 2 mL H_2SO_4 (1.0 mol L^{-1}), 3 mL of KI - ascorbic acid reagent and 1 mL Phen (0.05% m/v) were added. The test solution was diluted to 25 mL with de ionized water and shaken well with 5 mL MIBK (1:1v/v) for 2 min. After equilibrium, the floated complex ion associate between the two phases was separated out and re-dissolved in acetone (3 mL) acidified with H_2SO_4 (0.1 mol L^{-1}) and its absorbance was finally measured at 490 nm against the reagent blank.

Results and Discussion

Absorption UV visible spectra of developed colored complex species

In acid medium ($0.2 - 2 \text{ mol L}^{-1}$) and in the presence of an excess of iodide, bismuth forms the orange yellow complex BiI_4^- .¹⁵ The absorption spectrum (Figure 1) of the bismuth(III) iodide complex $[\text{BiI}_4]^-$ exhibits an intense maximum at 337 nm ($2.045 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and a less intense peak at 465 nm ($3.06 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) Figure 1. On mixing tetraiodobismuth(III) complex with the reagent $\text{TZ}^+\cdot\text{Cl}^-$ or Phen in H_2SO_4 (1.0 mol L^{-1}) and shaking for few minutes with chloroform (1:1v/v), orange red complex ion associates were developed in the organic phases.

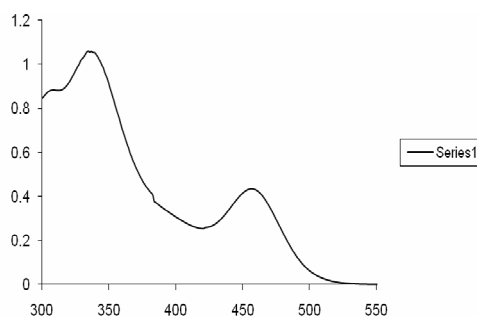


Figure 1. Absorption spectrum of the complex anion $[\text{BiI}_4]^-$ in water

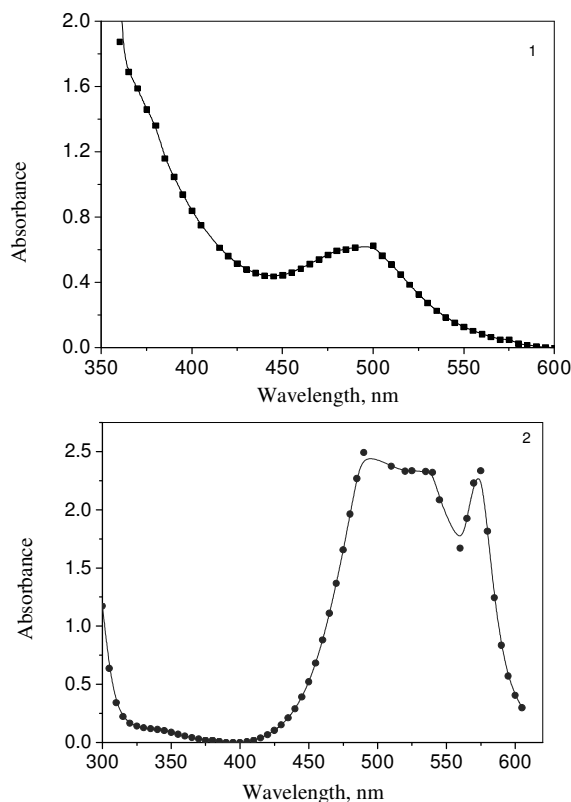


Figure 2. Absorption spectra of the developed complex associates $[Tz]^+.[BiI_4]^-$ in acetone - chloroform (1) and $[Phen]^+.[BiI_4]^-$ in acetone (2)

The absorption spectra of the developed yellow colored species of $[BiI_4]^-$ with Tz^+Cl^- in acetone - chloroform (1) and Phen in acetone (2) after extraction with MIBK and dissolving the colored scum are shown in Figure 2. The spectra of the associates of $[BiI_4]^-$ with Tz^+Cl^- in acetone - chloroform and the floated scum of Phen in acetone showed maximum absorbance at 500 nm and 490 nm, respectively.

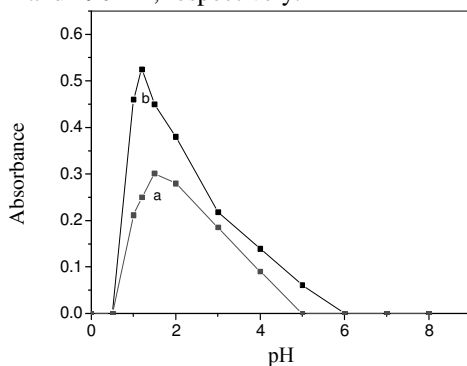


Figure 3. Influence of pH on the extraction of the complex ion associates $[Tz]^+.[BiI_4]^-$ in acetone-chloroform (1:1 v/v) (a) and $[Phen]^+.[BiI_4]^-$ in acetone (b)

Influence of analytical parameters on bismuth(III) extraction

The influence of pH of the aqueous phase on the extraction of the complex ion associate of bismuth(III) with the reagents $\text{Tz}^+\cdot\text{Cl}^-$ and Phen was studied by measuring the absorbance of the extracted complex ion associates in the solvent system acetone - chloroform (1:1v/v) and acetone at 500 and 490 nm, respectively. The final pH of each aqueous solution was adjusted with dilute HCl and/or NaOH before the extraction. The results are demonstrated in Figure 3. Maximum extraction of the produced ion associates were achieved at pH ~1-2. At pH ~1-2, bismuth(III) ions are able to form the stable complex anion $[\text{BiI}_4]^-$ which in turn form soluble ternary complex ion associates with $\text{Tz}^+\cdot\text{Cl}^-$ and Phen in non polar solvents. At pH > 2, a significance decrease in the absorbance of the extracted species was achieved and attributed to the decrease in the complex formation of the complex anion $[\text{BiI}_4]^-$ and also the hydrolyzed species BiOH^{2+} or BiO^+ or BiOCl . Formation of non extractable species of bismuth(III) in the organic solvents at pH > 2 may also account for the observed trend.

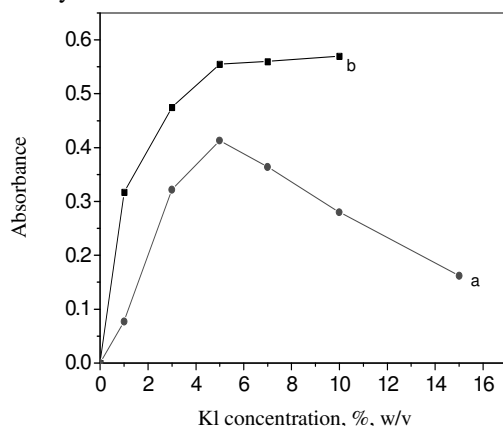
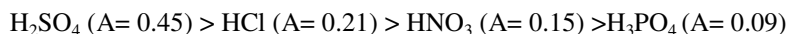


Figure 4. Effect of KI on the extraction of the complex ion associates $[\text{Tz}]^+ \cdot [\text{BiI}_4]^-$ in acetone - chloroform (a) and $[\text{Phen}]^+ \cdot [\text{BiI}_4]^-$ in acetone (b)

The influence of mineral acids *e.g.* HCl, H_2SO_4 , HNO_3 and H_3PO_4 in the concentration range 0.05-2.0 mol L^{-1} was examined as extraction media for the extraction of bismuth(III) with $\text{Tz}^+\cdot\text{Cl}^-$ and Phen in the presence of KI-ascorbic acid mixture. The absorbance (A) of the developed extracted colored species in the organic phase increased in the following order:



and maximum extraction was achieved in H_2SO_4 (0.1 mol L^{-1}). Thus, sulfuric acid at concentration 0.1 mol L^{-1} was adopted in the subsequent work.

The influence of KI concentrations on the formation and extraction of the ion associate of tetraiodobismuthate(III) with $\text{Tz}^+\cdot\text{Cl}^-$ and Phen was critically investigated and the results are demonstrated in Figure 4. Maximum absorbance and extraction of the formed complex ion associates were achieved at KI concentration up to 5% (w/v) followed by a sharp decrease at higher KI concentration. At KI concentration > 5%, significant decrease in the absorbance was noticed at 500 nm for $\text{Tz}^+\cdot\text{Cl}^-$. This behavior is most likely attributed to the possible formation of binary complex ion associate between iodide ion and the $\text{Tz}^+\cdot\text{Cl}^-$ reagent

forming the ion associate $TZ^+.I^-$ which competes effectively with extraction of the complex anion $[BiI_4]^-$ with $Tz^+.I^-$ reagent. On the other hand, KI may be oxidized by areal oxidation to iodine which also extracted onto the organic phase and competes with $[BiI_4]^-$ with $TZ^+.I^-$ associate. The atmospheric oxidation of iodide ion was minimized by ascorbic acid (1% w/v) in the test aqueous solution. In the case of 1, 10 phenanthroline reagent, maximum extraction was achieved at KI concentration of 5% (w/v) and remained constant (Figure 4).

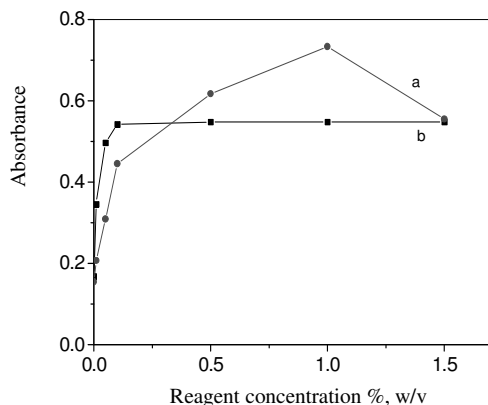


Figure 5. Effect of concentration of the reagent Tz^+Cl^- (a) and Phen (b) on the extraction of the produced complex ion associates of tetraiodobismuthate

The influence of the reagents Tz^+Cl^- and Phen concentrations on bismuth(III) extraction from the iodide media was investigated and the results are shown in Figure 5. Maximum absorbance was achieved at 1% (w/v) Tz^+Cl^- concentration followed by a sharp decrease at higher reagent concentrations. The increase in the uptake of the developed ion associate at 1% (w/v) Tz^+Cl^- concentration may be assigned to the ease of formation of the complex ion associate of Tz^+Cl^- with $[BiI_4]^-$.

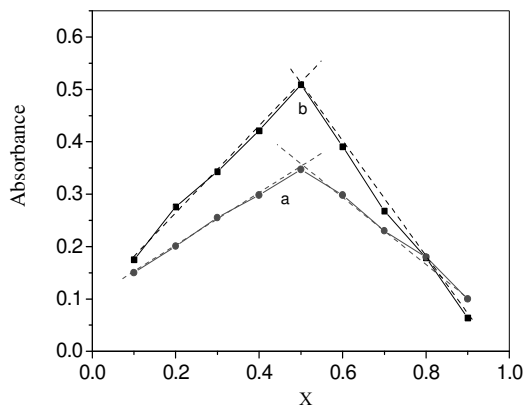


Figure 6. Jobs continuous variation plot for the complex ion associate of bismuth(III) with the ion pairing reagent $Tz^+.Cl^-$

The absence of any competition from other co - existence species in the extraction media may also account for the observed trend. At Tz^+Cl^- concentration $> 1%$ (w/v), the formation of the binary ion associate between iodide ion and the reagent Tz^+Cl^- may be

enhanced and competes with the associate of $TZ^+.Cl^-$ with $[BiI_4]^-$. For Phen reagent, maximum extraction of its associate with $[BiI_4]^-$ was achieved at 0.01% (w/v) reagent concentration and remained constant.

A variety of organic solvents *e.g.* methylisobutylketone (MIBK), *n*-hexane, chloroform, toluene, diethylether and ethylacetate was tested for the extraction of the ternary complex ion associates of bismuth(III) with $Tz^+.Cl^-$ and Phen using general recommended procedures. Both MIBK and the solvent system acetone- chloroform (1:1v/v) effectively extracted the ion associates of bismuth(III) with $Tz^+.Cl^-$ and Phen. The associate of $[BiI_4]^-$ with Phen was floated onto MIBK and the he floated layer (scum) was re dissolved in acetone and its absorbance at 490 nm was measured. The stability of the extracted ion associates was also tested by measuring their absorbance at various time intervals. The extracted complex ion associates were found stable for up to 24 h day light and stable for 3 h in direct sunlight.

Figure of merits of the developed analytical methods of bismuth(III) extraction

Under the optimum experimental conditions, the molar absorptivity of the ion associates of bismuth(III) with $Tz^+.Cl^-$ and Phen at 500 and 490 nm were found equal $1.74 \pm 0.02 \times 10^4$ and $2.14 \pm 0.002 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. Beer's law plots were obeyed in the concentration range 0.02-15 and 0.05-17 $\mu\text{g mL}^{-1}$ bismuth (III) using the reagents $Tz^+.Cl^-$ and Phen in aqueous iodide media, respectively. The Sandell's sensitivity index¹⁶ of the associate of bismuth(III) with $Tz^+.Cl^-$ at 500 nm was $0.063 \mu\text{g cm}^{-2}$, while for bismuth(III) - Phen associate at 490 nm it was found equal $0.074 \mu\text{g cm}^{-2}$, respectively. Least square analysis of the studied concentration range of bismuth(III) using $Tz^+.Cl^-$ and Phen yielded the following regression equations:

$$A_{500} = 0.07894C - 0.0129 \quad (1)$$

$$A_{490} = 0.09078C + 0.0119 \quad (2)$$

Where, C is the bismuth(III) concentration ($\mu\text{g mL}^{-1}$) with correlation coefficients (R) in the range 0.998-0.999. The effective concentration range of bismuth(III) as evaluated from Ringbom's plots¹⁵ are the established standard adopted to know the optimum range of effective concentration for systems that obeyed Beer's law. The plots drawn between $\log C$ of bismuth(III) and $1-T$, where T is the transmittance have sigmoid shape with linear segments at intermediate absorbance and concentration range of 0.06-12 and 1-15 $\mu\text{g mL}^{-1}$ bismuth(III) with $Tz^+.Cl^-$ and Phen, respectively.

The value of the lower limit of detection ($LOD = 3S_{y/x}/b$)¹⁷ where, $S_{y/x}$ is the standard deviation of y -residual and b is the slope of the calibration plot were found equal 0.008 and 0.009 $\mu\text{g mL}^{-1}$ bismuth(III) for the complex ion associates of $Tz^+.Cl^-$ and Phen, respectively. The LOD could be improved to lower value by increasing the sample volume of the aqueous phase containing trace or ultra trace concentrations of bismuth(III) and $Tz^+.Cl^-$ or Phen under the optimum experimental conditions. The relative standard deviation of five measurements, at 2 $\mu\text{g mL}^{-1}$ bismuth(III) employing the reagent $Tz^+.Cl^-$ and Phen was 2.1 ± 0.3 and 2.3 ± 0.16 , respectively. The figure of merits (LOD, linear range, RSD) of the procedure was better than compared successfully with many of the reported spectrometric methods⁹⁻¹¹. The time consuming on the developed method was compared successfully with some of the reported methods¹² confirming its precision.

Characterization of the complex ion associate of bismuth (III) with $TZ^+.Cl^-$ and Phen

The chemical composition of the formed complex ion-associates of bismuth(III) with the reagents $Tz^+.Cl^-$ and Phen was determined by Jobs continuous variation method¹⁸ and the results

are demonstrated in Figures 6 and 7, respectively. A 1:1 molar ratio of bismuth(III) to Tz^+Cl^- or Phen in their complex ion associates was obtained. The stoichiometry of the associates were confirmed by plotting $\log K_D$ versus $\log [R]$ according to the following equation^{19,20}:

$$\log D_{\text{Bi}} = \log K_D + \log \beta + \log [R] \quad (3)$$

Where, $R = \text{Tz}^+\text{Cl}^-$ or Phen and D is the distribution ratio of bismuth(III) at the initial concentration ($1 \times 10^{-6} \text{ mol L}^{-1}$) in the aqueous iodide media (pH 1-2) at various reagent (R) concentrations ($1.0 - 40.0 \times 10^{-5} \text{ M}$). The plots of $\log D_{\text{Bi}}$ versus $\log [R]$ were found linear (Figures 7 & 8) with a slope in the range 0.91-0.98 confirming the formation of 1:1 molar ratio of bismuth(III) to reagent.

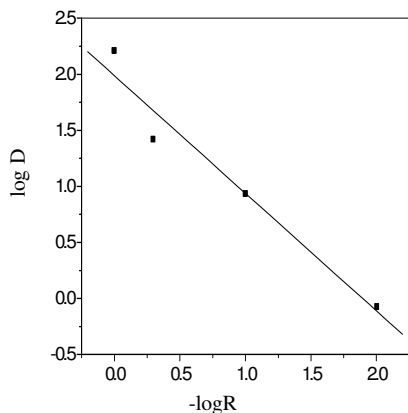


Figure 7. Plot of $\log D$ versus $\log [\text{Tz}^+\text{Cl}^-]$ of bismuth(III) extraction from aqueous KI medi at pH 1.2 into the organic phase.

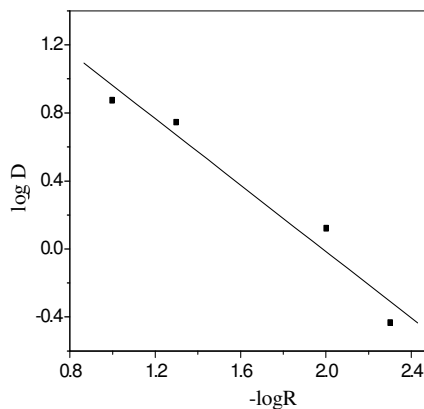


Figure 8. Plot of $\log D$ versus $\log [\text{Phen}^-]$ of bismuth(III) extraction from aqueous KI media at pH 1.2 onto the organic phase.

The solid complex ion associate of bismuth(III) with Tz^+Cl^- was isolated from the organic phase after with rotary evaporator. The produced complex associates $[\text{Tz}^+\text{BiI}_4^-]$ and $[\text{Phen}^+\text{BiI}_4^-]$ were then characterized from their elemental analysis. Analytical data for $[\text{Tz}^+\text{BiI}_4^-]$: Found: C=22.79, H=1.54, N=5.62, I=50.63; Calculated for $\text{C}_{19}\text{H}_{15}\text{N}_4\text{BiI}_4$: C=22.52, H=1.48, N=5.53, I=49.62. Analytical data for $[\text{Phen}^+\text{BiI}_4^-]$: Found: C=20.79, H=0.92, N=3.1, I=54.23; calculated for $\text{C}_{16}\text{H}_8\text{N}_2\text{BiI}_4$: C =20.4, H=0.85, N=2.9, I=53.3. These data confirmed the formation of 1: 1 molar ratio of bismuth(III) to the reagent Tz^+Cl^- or Phen achieved from the plot of $\log K_D$ versus $\log [R]$ by the electronic spectra^{19,20}. The IR spectra of the reagent Tz^+Cl^- , Phen and their isolated solid ion associates recorded separately in KBr discs showed the characteristic vibrations at 1636 (s), 1608 and 450 cm^{-1} which are safely assigned to $\nu(\text{N-N})$, $\nu(\text{C}=\text{N}) + (\text{C-N})$ and $\nu(\text{Bi-I})$ vibrations²¹, respectively confirming the proposed chemical structures of the developed associates.

Effect of diver's ions on the absorbance of the developed colored species of bismuth(III)

The influence of a relatively high excess (1 mg) of some diver's ions which are often accompanied with the analyt ion *e.g.* Li^+ , Na^+ , K^+ , Ba^{2+} , Ca^{2+} , Cu^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Zn^{2+} , Hg^{2+} , Cr^{3+} , SO_4^{2-} , Cl^- , Br^- and PO_4^{3-} on the extraction of the ion associate of bismuth(III) with the reagent Tz^+Cl^- was investigated. The tolerance limit (w/w) was set as the amount of foreign ion causing an error $\pm 3\%$ in the extraction. A percentage recovery of $96 \pm 1.5\%$ with a standard deviation of ± 0.3 was achieved. The ions Cu^{2+} , Cd^{2+} , Hg^{2+} , Pd^{2+} , Cl^- and

Br⁻ are interfered seriously. Moreover, the solution must be free from large amounts of thallium (I), tin, arsenic, antimony, gold, silver, platinum and from elements in sufficient quantity to color the solution *e.g.*, nickel.

Analysis of bismuth in water samples

The validity of the proposed Tz⁺.Cl⁻ method for bismuth(III) determination at trace concentrations spiked to various (tap, lake and wastewater) water samples was tested by comparison with the results obtained by inductively coupled plasma mass spectrometry (ICP-MS). The tested water samples (0.5 L) were collected, filtered through a 0.45 µm membrane filter and adjusted to pH 2. An accurate amount (0.0-15 µg) of bismuth(III) species were spiked individually into the water sample (0.5-1.0 L) and shaken well following the recommended procedures. The extracted bismuth(III) species were determined with the aid of the standard curve constructed under the same experimental conditions as described earlier. The data obtained are summarized in Table 2. The *F* (0.075) and *t* (1.91) tests at 5 µg mL⁻¹ bismuth(III) determined by the developed method and by the standard dithizone method¹⁷ showed no significant differences in accuracy.

Table 2. Analysis of bismuth(III) different water samples

Water sample	Bi(III) added, µg mL ⁻¹	Bismuth(III) found, µg mL ⁻¹
Tap water	10	9.7±0.032
Lake water	10	10.2±0.19
Wastewater	10	9.76± 0.31

Conclusion

The developed extractive spectrophotometric procedures for bismuth(III) determination in aqueous media does not involve any stringent reaction conditions and provided simple and inexpensive approach for bismuth(III) determination. The developed ion associates are stable and short time is needed in the determination step of bismuth(III) in water. Both methods are applicable for bismuth(III) determination in fresh water. Thus, the method can certainly be placed among the most sensitive ones. Work is continuing for application of the developed methods for the chemical speciation of bismuth(III & V) in environmental water samples.

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